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SHORT COMMUNICATION

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Preparation and stability of copper particles formed using the template of hyperbranched poly(amine-ester)

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Abstract The sixth-generation hydroxyl-ended hyperbranched poly(-amine-ester) (G6-OH) was investigated as template in formation and stabilization of copper nanoparticles. Ultra-violet spectra and transmission electron microscope were adopted to characterize absorption properties of G6-OH $(Cu^{2+})_n$ complex and the morphology of the formed particles $(G6\text{-}OH(Cu)_n)$, respectively. The template and stabilization functions of G6-OH were compared with di-block copolymer micelles and dendrimers having similar structure. It was found that the hyperbranched polymers could act as the templates for the preparation of copper particles. The size of the formed copper particles increased with Cu^{2+}/Gn-OH molar ratio. Besides, the oxygen influenced the chemistry stability of copper particles greatly.

Keywords Hyperbranched poly (amine-ester) · Copper particles · Template

Introduction

Dispersing metal and semiconductor nanoparticles into liquid mixtures are attracting more attention in seeking homogenous catalyst systems with extensive potential applications. Ten years ago, Valetsky and Bronstein et al. [1–9] reported the formation and stabilization of inorganic particles in aqueous through the micelle process of linear di-block copolymers. Some of the noble metal and semiconductor nanoparticles were successfully prepared. In the micelle process, the di-block polymers formed into multi-molecular micelles, in which the blocks in the core site could coordinate with ions (or other compounds) while the blocks in the periphery could maintain solubility or dispersion in the liquid medium. After reduction or other chemical conversion, the coordinated ions could be changed to metal or other particles, and then trapped inside the micelle. Obviously, these micelles worked as nanoreactors for nanoparticle formation. At the same time, the periphery blocks of micelle not only prevent the agglomeration of nanoparticles, but also improved the dispersion of the encapsulated particles in liquid medium.

Differing from linear polymers the appearing dendrimers have characteristics, including tree-like and intra-molecular void structure, inter-molecular tangling-free in solution, and a large number of branching points and end-groups. In solution, dendrimers could act not only as monomolecular micelles, but also as carriers or templates for nanoparticles. Currently, the investigations of dendrimers have been mentioned in the field of drug carriers [10–12], catalysts [13–16], host-guest materials [17–20], preparation of metal and ceramic nanoparticles [21–25]. In the preparation of metal nanoparticles, the metal ions first coordinated with groups (e.g. amino groups) interior dendrimer, and then were reduced to metal particles. The trapping effect of dendrimer arms could contribute toward the dispersion and stability of the encapsulated particles.

The above introductions revealed the similarity between dendrimer and linear diblock polymer process in preparing metal nanopartilces. Their difference might lie in the metal coordination process, the size of obtained metal particles or their further functionalization. However, the practical applications must be taken into account in the preparation of template polymer. For dendrimers, the key limits should be the difficulty in large-scale synthesis. The hyperbranched polymer (HBP) is a polymer that has the structure and property which is most similar to the dendrimer, and could be synthesized in a large-scale easily through one-step polycondensation of AB_x-type monomers. HBPs may contain isomers and have a less-ordered structure or a little larger poly-diversity in comparison with dendrimers. Regardless, it should be reasonable to inquire about HBPs‘ properties in the formation and stability of metal particles. Such attempts are also consistent to the current trends in replacing dendrimer with HBPs in some fields [26]. In this work, the formation and the stability of copper nanoparticles were investigated using the sixth generation hydroxyl terminated hyperbranched poly(amine-ester) (HPAE, G6-OH) as template. The obtained results were compared with those of di-block polymers and dendrimers.

Experimental section

Materials

All chemicals were analytical grade. Diethanolamine (DEA), methanol (MeOH) and methyl acrylate (MA) were purified by vacuum distillation before being used. Copper chloride ($CuCl_2$, 99.99%) and sodium borohydride ($NaBH_4$, 99.99%) were used as received. Organic-free de-ionized water was used throughout all the experiments.

Synthesis of the hyperbranched poly(amine-ester) and copper nanoparticles

Hyperbranched poly(amine-ester) HPAE G6-OH was synthesized according to previous literature [27]. The preparation of copper particles proceeded as follows: (1) variable amount of $CuCl_2$(0.05–0.4 mol/l in aqueous solution) was added to the G6-OH HPAE aqueous solution (0.01 mol/l, calculated with the hydroxyl group as standard), and the mixture was stirred for 5 h to yield a solution of Cu^{2+}/G6-OH complex ions (G6-OH $(Cu^{2+})_n$). (2) $NaBH_4$ (in 0.1 mol/l aqueous solution of 0.03 mol/l NaOH) of threefold molar excess to $CuCl_2$ was added, and the mixture solution was vigorously stirred for 1 h under oxygen-free atmosphere at room temperature. After dialyzing the reduced mixture with a poly(ether sulfone) membrane, a solution of G6-OH encapsulated copper particle (G6-OH$(Cu)_n$) was obtained.

Characterization

The absorption of Cu^{2+}/G6-OH complex ions (G6-OH$(Cu^{2+})_n$) and the encapsulated copper particles in aqueous solutions were recorded on UV-vis spectrophotometer (Shimadzu UV-1601). The morphology of G6-OH$(Cu)_n$ particles were imaged on transmission electron microscope (TEM JEM200CX).

Results and discussion

UV-vis absorption properties of G6-OH(Cu^{2+}) complex ions

The absorption characteristics of Cu^{2+} coordinated with G6-OH were shown in Fig. 1. Due to the HPAE not having any photoactive group or charge transfer system, no absorption occurred at wavelengths ranging from 300 nm to 900 nm (Fig. 1a). In $CuCl_2$ solution without HPAE, Cu^{2+} mainly existed as complexes of $[Cu(H_2O)_6]^{2+}$ and the distortion of d–d transitions for Cu^{2+} in tetragonal to octahedral or square-planar ligand field resulted in a broad absorption band with λ_{max} at 810 nm (Fig. 1b) [28]. After G6-OH HPAE was added into $CuCl_2$ solution, the absorption at 810 nm disappeared and a new absorption at $\lambda_{max}=696$ nm appeared (Fig. 1c–e). The shift in λ_{max} was induced by the change of the ligands in Cu^{2+} complexes. In the G6-OH/$CuCl_2$ solution, the ligands coordinated with Cu^{2+} included H_2O and the tertiary amino units inside the HPAE molecule. Theoretically, the coordination ability

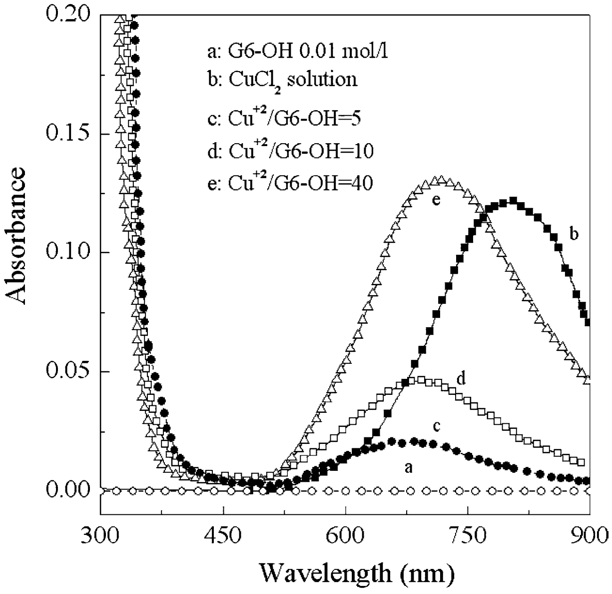

Fig. 1 UV-vis absorption of G6-OH(Cu^{2+}) complex ions with different Cu^{2+}/G6-OH molar ratio in aqueous solution

of H_2O is weaker than that of the tertiary amino units. So, the blue-shift absorption appeared when partly or all of the ligands in Cu^{2+} complex ions were converted from H_2O to tertiary amino units. Based on the previous report [29, 30], each Cu^{2+} ion could only coordinate with two amino groups. Therefore, another four coordination positions should be still occupied by weak coordinating ligands, such as water molecules or Cl^- . By increasing the molar ratio of Cu^{2+} /G6-OH, more Cu^{2+} ions were absorbed inside HPAE and the absorption intensity at $\lambda_{max} = 696$ nm enhanced.

UV-vis absorption of G6-OH(Cu)$_n$ particles

With the addition of $NaBH_4$, the blue-colored $CuCl_2$ solutions changed to golden brown gradually. The higher the Cu^{2+}/G6-OH molar ratio, the shorter the time required for the color change. The disappearance of G6-OH(Cu^{2+})$_n$ absorption at 696 nm indicated that the Cu^{2+} in G6-OH(Cu^{2+})$_n$ complex ions had reduced to zero covalent copper efficiently. In the case of G6-OH free system, the separate dark precipitates appeared and the solution turned colorless within 20 min after adding $NaBH_4$. However, the reduced solutions containing G6-OH still remained golden brown in color and in an homogenous state after passing longer than 11 h in an oxygen-free atmosphere. It could be concluded that the hyperbranched G6-OH provided an effective stabilization for Cu particles. The results were the same as those using dendrimers as templates [21].

The UV-vis absorption behavior of G6-OH(Cu)$_n$ solutions varied obviously with Cu^{2+}/G6-OH molar ratio (Fig. 2). The size of Cu particles formed in different Cu^{2+}/G6-OH ratio systems could be first detected from the difference in the UV-vis spectra. For G6-OH(Cu)$_n$ solution, whose Cu^{2+}/G6-OH molar ratio was 5, a monotonously increasing absorbance in nearly exponential slope toward shorter wavelength was observed. Together with absorption rising around 590 nm (Fig. 2a), the obtained Cu particles' size was regarded as smaller than 4 nm [31, 32]. While the Cu^{2+}/G6-OH molar ratio was adopted as 10 and 40, a Mie-plasmon peak emerged besides the nearly monotonously increasing absorbance mentioned above. The appearance of Mie-plasmon resonance peak at $\lambda_{max} = 570$ nm suggested that the size of the Cu particles was larger than 5 nm [32–35]. There were two type of particles in this reduced solution, some smaller than 4 nm, while the others were larger than 5 nm.

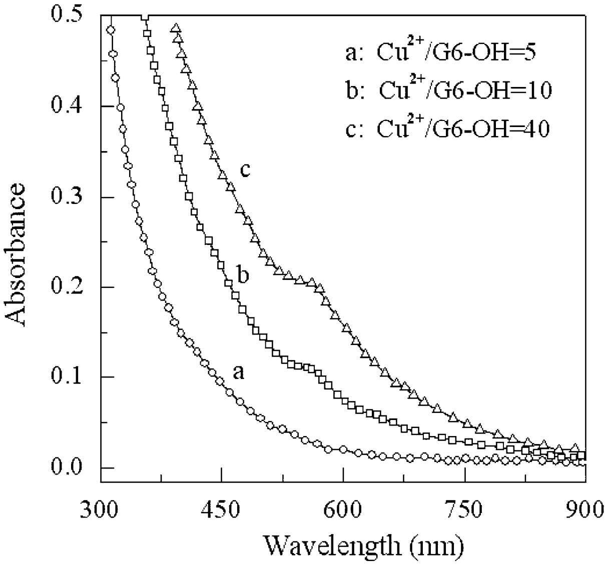

Fig. 2 UV-vis absorption of G6-OH(Cu)$_n$ solutions with different Cu^{2+}/G6-OH molar ratio after an hour from $NaBH_4$ addition

The change of absorption and aggregation in the formation of G6-OH(Cu)$_n$

The formation rate of copper particles could be inferred from the UV-vis absorption changes presented in Fig. 3. After adding reducing agent of $NaBH_4$ into oxygen-free solution of G6-OH and $CuCl_2$ in water, the absorption of the complex ion (G6-OH(Cu^{2+})$_n$) and its thorough disappearance within 10 min indicated that the copper ions could be reduced quickly and completely. The coordination of Cu^{2+} ions within G6-OH did not affect their reducing property. Also, that the absorption spectrum changed greatly with time revealed that the aggregation of copper particles developed gradually. At the initial stage (e.g. 10 min after adding $NaBH_4$), the monotonously increasing absorbance beginning 590 nm toward shorter wavelengths indicated that the size of

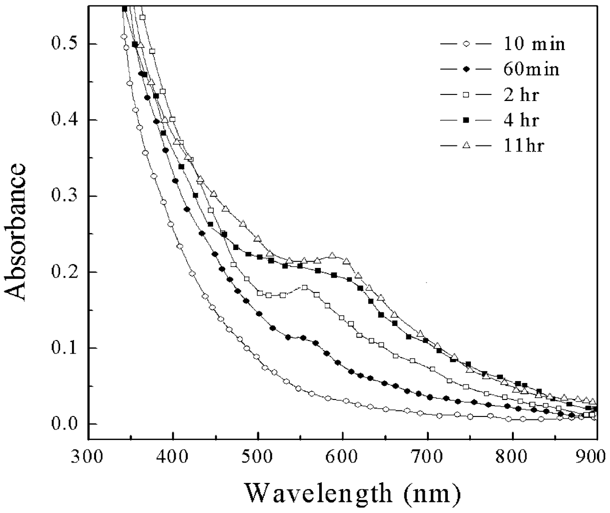

Fig. 3 The absorption spectra of the oxygen-free solutions after the addition of $NaBH_4$ (Cu^{2+}/G_6-OH = 10/1)

copper particles was smaller than 4 nm. Sixty minutes after adding $NaBH_4$, the Mie-plasmon resonance peak at $\lambda_{max} = 570$ nm showed that the size of the Cu particles was larger than 5 nm. With the passage of time, the Mie-plasmon absorption became stronger and the red shift occurred. These phenomena manifested the aggregation of copper particle to develop gradually in solution.

The morphology of copper particles

The size and morphologies of HPAE G6-OH and G6-OH$(Cu)_n$ particles could be directly estimated by TEM images shown in Fig. 4. As observed, the diameter of G6-OH ranged 30–70 nm, which was larger than the hydrodynamic diameter of the corresponding mono-dispersed G6-OH dendrimers (6.9 nm) with the same component [36]. This result could be attributed to HPAE G6-OH aggregation caused by hydrogen bonds among the peripheral hydroxyl groups. During TEM measurement, HPAE G6-OH flattened on the carbon support still in aggregation state. For the reduced systems, where the molar ratio of Cu^{2+}/G6-OH was 5, particle domains were observed in a distribution range of 10–25 nm. This domain size was larger than 4 nm, and was not consistent with the result inferred from UV-vis absorption in Fig. 2a. This difference resulted from the aggregation of the copper particles, and suggested that the particles tended to aggregate even though at lower Cu^{2+}/G6-OH ratio. If the Cu^{2+}/G6-OH molar ratio was increased to 10, domains of aggregated particles with a diameter about 50 nm were found. While Cu^{2+}/G6-OH was up to 40, the size of imaged domains became larger and ranged in scale of 80–120 nm. The aggregation extent increased with increasing Cu^{2+}/G6-OH molar ratio. Though the UV-vis absorption indicated copper nanoparticles smaller than 4 nm in solution, the morphology of dried particles was detected with difficulty by TEM. This case could be reasonably explained following the intrinsic aggregation tendency of nanoparticles. In this work, the imperfect structure of HPAE, the low reduction potential and the high reactivity of copper promoted the aggregation of copper clusters [37].

The size of noble metal nanoparticles (Pt, Au, Pd, Rh, Mo etc) prepared using linear di-block copolymer (Poly(ethylene oxide)-block poly(4-vinylpyridine), polystyene-block-poly(ethylene oxide), polystyene-block-poly-4-vinylpyridine), etc) through micelles process ranged from 2 nm to 100 nm [1–4, 38, 39]. The size of that obtained from dendrimer template with similar composition to G6-OH in this paper was 4 nm [37, 40]. These size differences might be mainly caused if the structure of HBPs was not as perfect as that of dendrimers and the micelle structure of the copolymer colloids.

The coordination of nitrogen with metal ions acted as the driving force of the formation of micellar structures. The characteristic of these micelles depended strongly on the metal compound, the molar ratio polymer: metal, block length, the type of the reducing agent, etc. [1, 2, 41–46]. It was known that not all metal compounds are able to induce micelle formation, as copper ions can not. Due to the fact that copper ions could coordinate with different amino groups and the lability of the formed

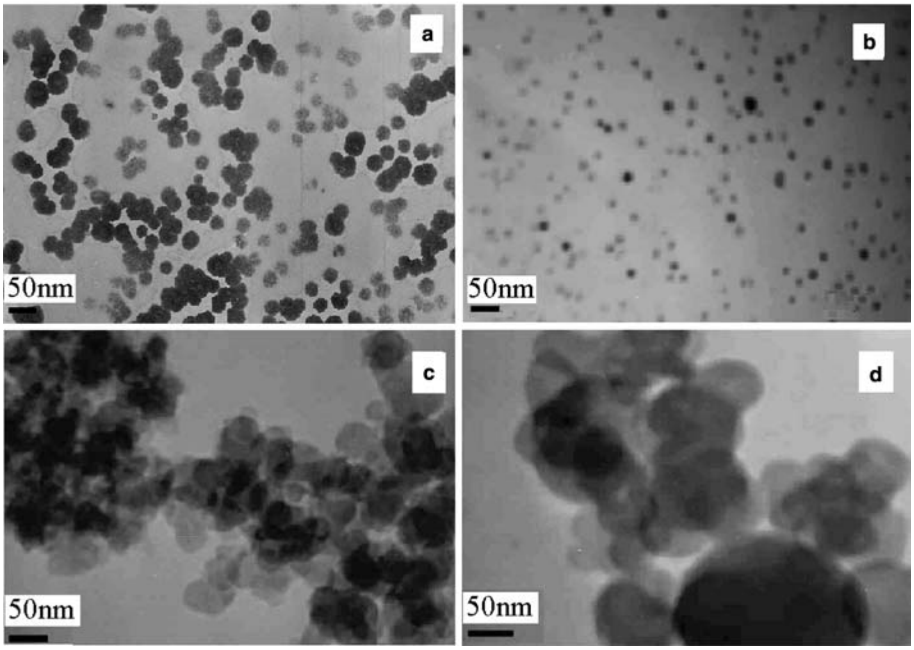

Fig. 4 The TEM of copper particles obtained from different Cu^{2+}/G6-OH ratio in the absence of oxygen, **a** G6-OH singly, **b** 5:1, **c** 10:1, **d** 40:1

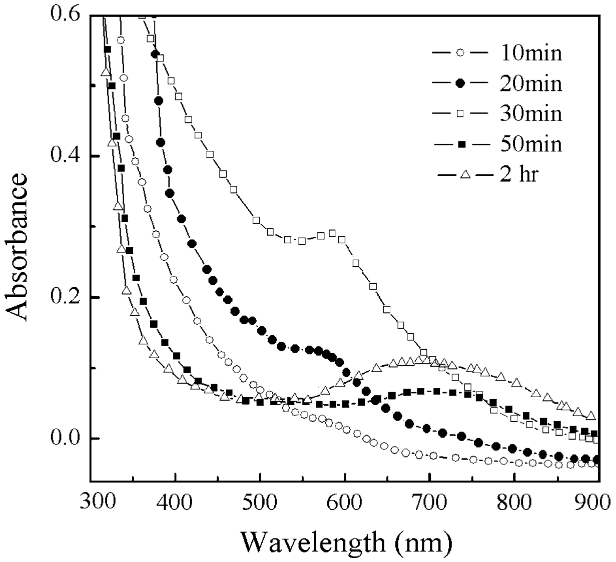

Fig. 5 The absorption spectra of solution containing G6-OH $(Cu^{2+})_n$ after reduction in oxygen existence $(Cu^{2+}/G_n\text{-}OH = 10/1)$

micelles, the linear di-block copolymer could not be used in the preparation of copper nanoparticles. What's more, the changing of solution conditions (pH or the surfactant etc) or block length would lead the nanoparticles to form into 200- to 500-nm-diameter polymer aggregates [4–6]. However, for the G6-OH, like dendrimers, the hyperbranched polymer first acted as the molecular template to let the ions cooperate with the tertiary amino units, then as stabilizer to prevent particles from agglomeration. The difference of HBP and dendrimers with block copolymer in preparation nanoparticles was the template function and the large number of branching points or end groups of the former. The most important aspect was that the many branching points and end groups could enhance the selectivity as catalysts and reactivity for other uses. Thus, concerning practical applications, it was still possible to induce the HBPs to act as the proper template and stabilizer candidates in the preparation of copper particles in solutions.

Influence of oxygen on the formation and stability of Cu particles

Oxygen greatly influenced the formation and stability of copper particles using G6-OH as template. The copper particles can be stable in an oxygen-free solution longer than 11 h. When the reduced solution was exposed to air environment, its UV-vis spectrum changed quickly (Fig. 5). If the reduced solution could stay brown in color only for 40 min, then its UV-vis absorption displayed the characters of original complex ions of G6-OH$(Cu^{2+})_n$. The zero covalent copper was converted to G6-OH$(Cu^{2+})_n$ complex ions. This observation showed the merit that the obtained copper particles could be oxidized easily in this case. Despite the fact that such instability should be avoided in preparing copper or other particles, such instability seemed to provide a novel catalyst system of quickly reversible oxidation–reduction circles based on metal-particles.

Conclusions

Cu^{2+} ions could form into G6-OH$(Cu^{2+})_n$ complexes through the coordination with the tertiary amino units inside G6-OH and was converted into copper nanoparticles in oxygen-free condition. With the ratio of Cu^{2+}/G6-OH increasing from 5 to 40 nm, the copper particles size could be controlled in range of 10–150 nm. In this process, G6-OH acted as both the templates and the stabilizers of copper particles. In comparison, the particles size obtained using G6-OH was larger than that using similarly structured dendrimers, and smaller than some of that prepared using linear di-block copolymer micelles. Also, the copper particle in G6-OH had higher aggregation tendency than that in dendrimer template or block copolymer micelles. If oxygen existed, the formed copper particles could be oxidized to Cu^{2+} easily.

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